

THE INVESTIGATION OF CERTAIN TYPES OF
SOUTH AFRICAN COALS, WITH SPECIAL REF-
ERENCE TO THEIR HIGH NITROGEN CONTENT

BY

VERNON BOSMAN

A.B., University of the Cape of Good Hope, South Africa, 1917

M.A., University of Cape Town, South Africa, 1918

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1922

URBANA, ILLINOIS



Reprinted from the South African Journal of Industries, May, 1923

3781

I29B

UNCLASSED

Dissertation

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ACKNOWLEDGEMENT

The author wishes to thank Professor S. W. Parr for his kind assistance and advice in compiling this thesis.

A STUDY OF SOUTH AFRICAN COALS.

WITH SPECIAL REFERENCE TO THEIR NITROGEN-CONTENT.

By VERNON BOSMAN* with S. W. PARR.

THIS work describes an investigation of certain types of South African coals, planned with a view to obtaining a more fundamental knowledge of the form in which nitrogen exists in coals. Almost all of the fourteen samples used may be looked upon as high nitrogen coals, five of them containing an average amount of over 2 per cent., as compared with an average of 1 to 1.5 per cent. in American coals.

Two general methods of attack were employed: (1) the distillation of coal in the presence of carbon dioxide,† and (2) the use of chemical reagents.

Tables 1 and 2 show a complete analysis of the coals as determined according to standard methods described in "Water and Fuel" analysis by Parr (1922).

THEORETICAL.

In the following investigations certain theoretical considerations regarding the origin of coal were made use of. In the first place, it is assumed that the accumulative vegetal matter, during its process of decomposition towards the formation of coal, is exposed to two fundamental agencies: (a) Biochemical or bacterial, and (b) dynamochemical.

TABLE I.—PROXIMATE ANALYSES OF SOUTH AFRICAN COALS.

Locality.	Laboratory Number.	Proximate Analyses.				Moisture Free.			Moisture and Ash Free.		Air Drying Loss.
		H ₂ O.	Vol. Mat.	Fixed Carbon.	Ash.	Vol. Mat.	Fixed Carbon.	Ash.	Vol. Mat.	Fixed Carbon.	
Utrecht Colliery, Natal.....	1	2.83	25.93	60.64	10.60	26.69	62.40	10.91	29.95	70.05	.22
Cambria Colliery, Natal.....	2	1.42	28.04	62.28	8.26	28.44	63.18	8.38	31.05	68.95	.23
S.A. Northfield Colliery, Natal.....	3	1.53	23.10	68.02	7.35	23.46	69.08	7.46	25.35	74.65	.17
Navigation Colliery, Natal.....	4	1.47	22.29	67.14	9.10	22.60	68.16	9.24	24.93	75.07	.21
Transvaal and Delagoa Bay, Witbank, No. 8	5	1.88	33.41	51.85	12.86	34.04	52.85	13.11	39.18	60.82	.36
Clydesdale Colliery, Blackhill, No. 2..	6	2.60	28.28	57.93	11.19	29.02	59.50	11.48	32.79	67.21	.12
Cassel Coal Coy., Blackhill, No. 1	7	1.93	29.98	57.61	10.48	30.58	58.73	10.69	34.24	65.76	.13
Steam Coal and Coke, Middelburg	8	1.94	27.99	54.09	15.98	28.54	55.17	16.29	34.10	65.90	.23
Coronation Colliery, No. 3.....	9	1.87	27.56	57.24	13.33	28.08	58.34	13.58	32.49	67.51	.16
Enyati Colliery, Natal.....	10	1.28	23.70	67.06	7.96	24.01	67.95	8.04	26.11	73.89	.31
Uitspan Colliery, Witbank, No. 10	11	1.81	25.47	58.07	14.65	25.93	59.15	14.92	30.48	69.52	.11
Clydesdale Colliery, No. 2.....	12	2.48	28.46	57.44	11.62	29.18	58.90	11.92	33.13	66.87	.19
Tavistock Coal and Coke Co., No. 6..	13	2.03	28.43	58.46	11.08	29.02	59.67	11.31	32.72	67.28	.27
African Freehold, Middelburg, No. 1	14	2.57	29.16	57.68	10.59	29.93	59.21	10.86	33.58	66.42	.32

* Abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois, 1922.

† From an unpublished thesis done at the University of Illinois: Carbon dioxide has no effect on the results in carbonization processes (F. B. Hobart, 1921).

TABLE 2.—ULTIMATE ANALYSES OF SOUTH AFRICAN COALS.

Locality.	Laboratory Number.	Ultimate Analyses.					Calorific Value.	
		S.	H ₂	Carbon.	N ₂	O ₂	Calories.	B. T. U.
Utrecht Colliery, Natal.....	1	1·58	4·45	70·70	2·12	7·72	6,952	12,334
Cambria Colliery, Natal.....	2	1·67	4·90	75·93	2·17	5·66	7,616	13,707
S.A. Northfield Colliery, Natal..	3	1·71	4·79	77·33	2·32	4·97	7,726	13,917
Navigation Colliery, Natal.....	4	1·72	4·64	76·30	2·17	4·60	7,606	13,695
Transvaal and Delogoa Bay, Witbank, No. 8.....	5	1·24	4·81	69·33	1·68	8·20	6,900	12,421
Clydesdale Colliery, Blackhill, No. 2	6	1·26	4·22	70·50	1·62	8·61	6,808	12,255
Cassel Coal Co., Blackhill, No. 1.	7	1·29	4·46	71·98	1·68	8·18	7,057	12,702
Steam Coal and Coke, Middelburg	8	·87	4·16	67·45	1·53	8·07	6,558	11,805
Coronation Colliery, No. 3.....	9	·88	4·80	68·18	1·67	9·27	6,787	12,119
Enyati Colliery, Natal.....	10	1·24	4·54	77·47	2·11	5·40	7,622	13,720
Uitspan Colliery, Witbank, No. 10	11	·84	4·23	68·43	1·61	8·43	6,645	11,960
Clydesdale Colliery, No. 2.....	12	1·40	4·33	69·86	1·60	8·61	6,797	12,232
Tavistock Coal Co., Witbank, No. 6	13	1·39	4·30	71·38	1·75	8·07	6,925	12,464
African Freehold, Middelburg, No. 11.....	14	·42	4·54	70·38	1·78	9·72	6,885	12,392

This theory is described and illustrated in a very thorough and extensive bulletin by David White, Thiessen, and Davis.*

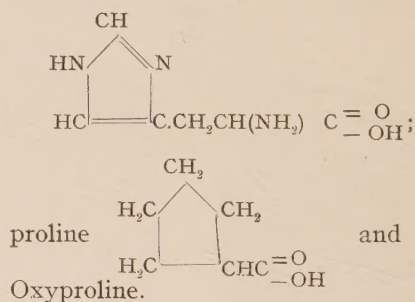
Secondly, it is assumed that the nitrogen in coal originates from the protein in the plant from which the coal was formed. Coming from the plant it is certain that the nitrogen is of organic and not of inorganic origin. It is true that certain plants contain alkaloids in which the nitrogen is bound differently in the molecule from protein, but it is not likely that these compounds play any important part in coal formation, for such plants are not common and are small in bulk. All writers who have made a study of the nitrogen in coal have believed that protein is its true origin.†

Decomposition Products of Proteins.

Proteins in the presence of hydrolysing agents readily decompose, and yield as products of decomposition the following groups of compounds:—

- (1) Amino acids, which include monamino and diamino carboxylic acids.
- (2) Acid amides.

- (3) Heterocyclic compounds, such as histidine, having the formula



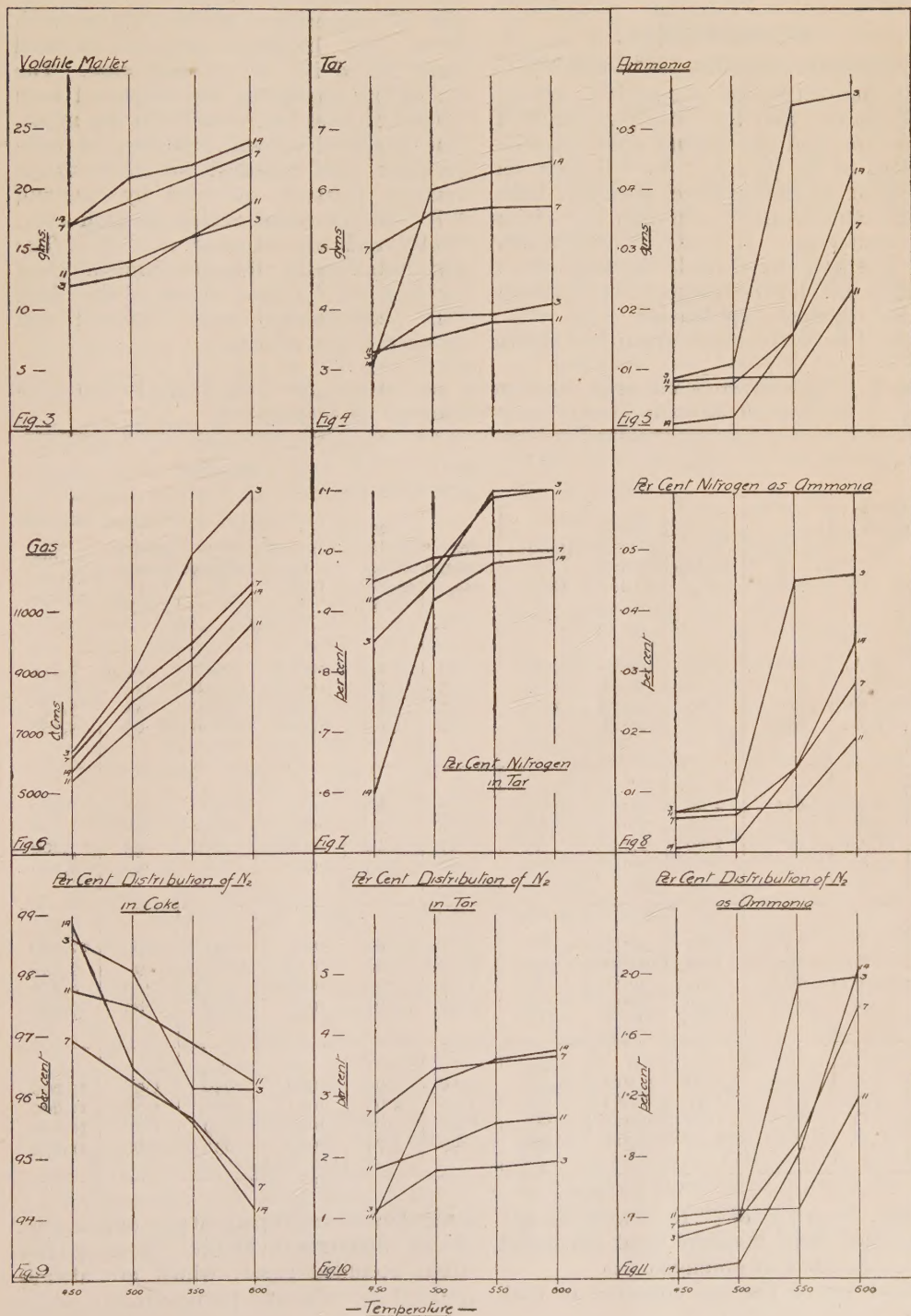
Now, when proteins are exposed to the natural agencies which are supposed to exist in the formation of coal, we would expect hydrolysis to be brought about by bacterial action, and, as a result, the products of decomposition would be brought down in the coal mass. These compounds either remain unaffected, and in that case will be present in the coal as such; or they may recombine to form new compounds, or, thirdly, they may decompose and pass off from the coal-forming mass as ammonia or nitrogen.

* White, D., Thiessen, R., Davis, C.: "The Origin of Coal," B. 38, Bur. of Mines (1913); Thiessen, R.: "Structure in Paleozoic Bituminous Coals," B. 117, Bur. of Mines (1920).

† Terres, E., *Chem. Ztg.*, 39-73 (1915); Smith, W., *J.S.C.I.*, 10, 975 (1891); Anderson, W. C., and Roberts, J., *J.S.C.I.*, 17, 1013 (1896); Harger, *J.S.C.I.*, 33, 389-392 (1914); Bone, W.: "Coal and its Scientific Uses."

— The Distillation of Coals between 450°C and 600°C —

— Using 100gm. Samples —



These theoretical considerations form the basis of the work which is to follow.

EXPERIMENTAL.

A.—Distillation between 450°C. and 500°C.

In the distillation of coal it is universally known that the respective yields of coke, tar, and gas depend upon the conditions of the process. Such factors, for instance, as temperature, pressure, time, and contact surfaces will alter the yields in appreciable amounts. Consequently all attempts were made to keep other factors, besides the temperature, constant in the different experiments.

For this purpose the apparatus shown

in figure 1 was used. The furnace was heated electrically. Figure 2 shows the rise in temperature of the furnace with time. One hundred grammes of coal were placed in "A" in each case. The air in the apparatus was displaced with carbon dioxide before each run was made. The gas evolved with the rise in temperature was collected in "E" under reduced pressure, obtained by lowering "F" to the same extent in each case. Water and tar collected in "B." The gas, after being filtered through glass wool in "C," passed through the flask "D" containing normal sulphuric acid to absorb the ammonia.

TABLE 3.—QUANTITATIVE YIELDS OF, PERCENTAGE OF NITROGEN, AND PERCENTAGE DISTRIBUTION OF NITROGEN IN COKE, TAR, AND AMMONIA ON DISTILLATION.

Experiment No.	Coke.			Tar.			Ammonia.			Gas.	
	Amount in Gms.	Percentage N ₂	Percentage Distribution of N ₂	Amount in Gms.	Percentage N ₂	Percentage Distribution of N ₂	Amount in Gms.	Percentage N ₂	Percentage Distribution of N ₂	Amount in Cubic Centimeters.	
Temp. 450° C.	3 A.	88.	2.70	98.60	3.23	.85	1.12	.0085	.0067	.27	6,325
	7 B.	83.	2.03	96.94	5.00	.95	2.71	.0070	.0058	.34	6,150
	11 C.	87.	1.85	97.75	3.30	.92	1.82	.0081	.0067	.41	5,400
	14 D.	83.	2.07	98.85	3.10	.60	1.09	.0010	.0008	.05	5,700
Temp. 500° C.	3 E.	87.	2.68	98.07	3.90	.95	1.80	.011	.009	.38	8,900
	7 F.	81.	1.89	96.23	5.60	.99	3.46	.0075	.0062	.39	8,400
	11 G.	86.	1.80	97.48	3.53	.97	2.14	.0087	.0072	.45	7,200
	14 H.	79.	2.07	96.47	6.00	.92	3.23	.0021	.0017	.10	8,000
Temp. 550° C.	3 I.	84.	2.67	96.13	3.92	1.10	1.84	.054	.045	1.93	12,900
	7 J.	79.	1.93	95.62	5.70	1.00	3.55	.016	.014	.9	9,950
	11 K.	84.	1.84	96.88	3.80	1.09	2.56	.0088	.0073	.46	8,450
	14 L.	78.	2.10	95.57	6.30	.98	3.61	.016	.014	.82	9,400
Temp. 600° C.	3 M.	82.5	2.70	96.12	4.10	1.10	1.94	.056	.046	1.98	15,000
	7 N.	77.	1.91	94.53	5.70	1.00	3.65	.034	.028	1.79	11,900
	11 O.	81.	1.78	96.25	3.82	1.10	2.63	.023	.019	1.19	10,600
	14 P.	76.	2.12	94.16	6.46	.99	3.74	.043	.035	2.04	11,650

The contents of "D" were finally redistilled into standard acid for exact determinations of ammonia.

Analyses of the gas collected in each

case showed small percentages of nitrogen. These amounts evidently arose, partly from occluded gases, which are always present in coals, and partly from a slight

decomposition of ammonia. The amounts were small and consequently were neglected in the calculations.

Table 3 gives the quantitative yields of coke, tar, ammonia, and gas at temperatures of 450° C., 500° C., 550° C., and 600° C. obtained from 100 grammes of coal; and the percentage of nitrogen in each, as determined by the Kjeldahl-Gunning method, and the percentage distribution of nitrogen at these temperatures.

These results are also shown graphically in figures 3-11. Here we have endeavoured to show the behaviour of each coal separately as it passes from one temperature to another. Thus, figures 3-6 show the respective amounts of volatile matter, tar, ammonia, and gas, of each coal at the different temperatures; figures 7 and 8 the percentage of nitrogen in tar and ammonia at each temperature; and figures 9-11 the percentage distribution of nitrogen in the coke, tar, and ammonia at the respective temperatures.

A comparative study of these graphs is very useful and brings to light some very interesting facts regarding the constitution of coal. Thus, in figure 4, showing the quantities of tar given off, there is a decomposition of coal at 450° (or slightly above), yielding a rapid evolution of tar. At 500° most of the tar has been given off in all cases except that of No. 11, which continues gradually up to 550° C. before a lag in the curve is observed. On the other hand, in the case of ammonia (fig. 5), the rapid evolution of ammonia only begins at 500° C. This again is true in all cases, except that of No. 11, when the rapid evolution only begins at 550° C. Thus, in all cases it is shown conclusively that the molecule containing the bulk of the nitrogen only starts decomposing after all the tar-producing constituents have been removed. Furthermore, this ammonia decomposition follows directly after the breaking down of the tar-forming constituents. A small portion of the nitrogen, however, comes off with the tar and is closely associated with it.

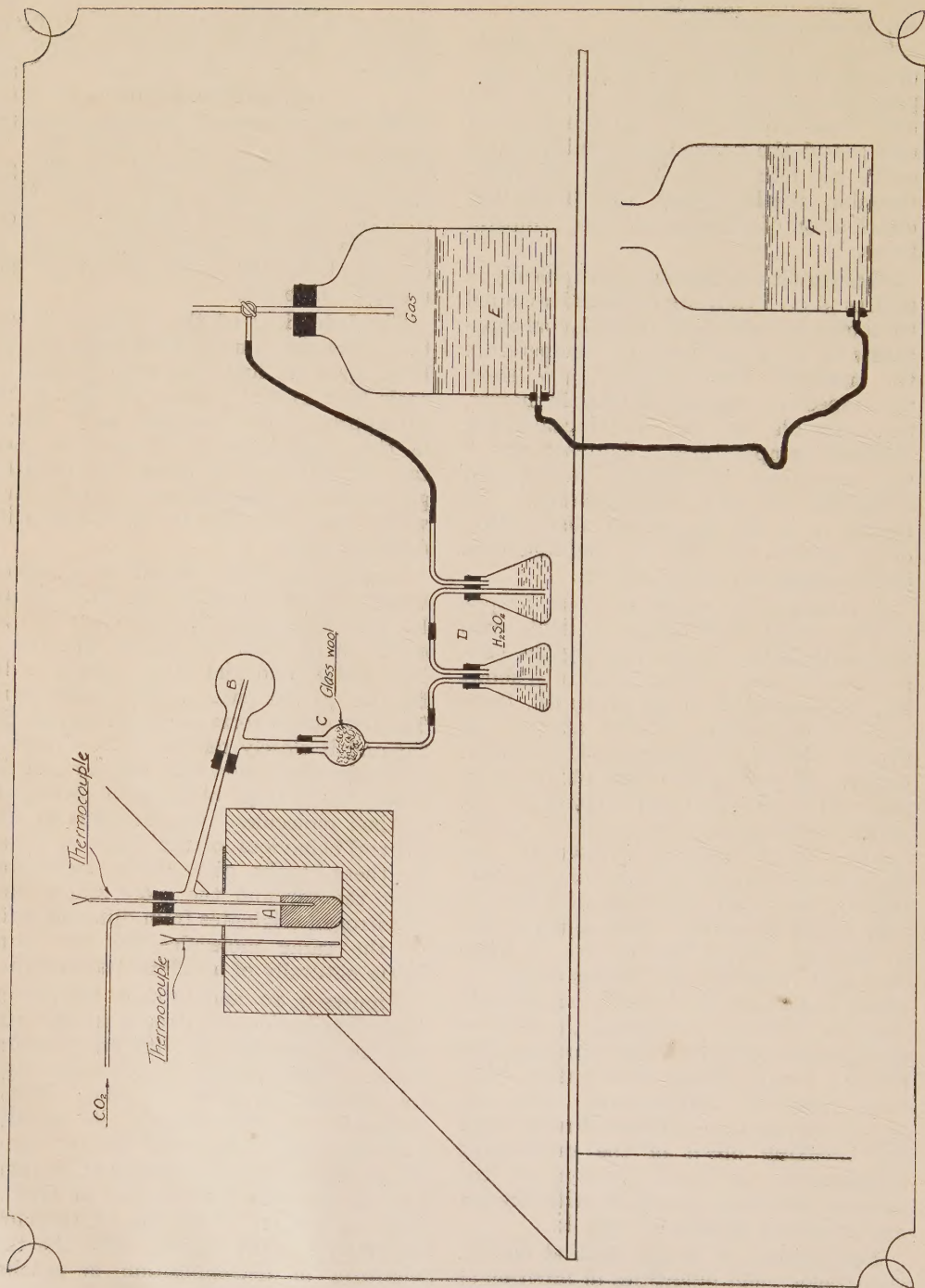
Furthermore, it is seen that at 600° C. these coals yield quantities of nitrogen as ammonia in direct proportion to the

total quantity of original nitrogen in the coal. Thus in figure 6, Coal No. 3, containing the highest percentage of nitrogen, liberates also the greatest amount of nitrogen as ammonia at 600° C. Coals No. 14, No. 7, and No. 11 follow in order. This, however, is not the case at lower temperatures. At 500° C. coal No. 11 liberates a greater amount of nitrogen than coal No. 7, and coal No. 7 more than coal No. 14. This is evidence to show that this part of the nitrogen-content is distinct from the main portion of the nitrogen molecule.

The behaviour of the nitrogen in the tar shows the same characteristic (fig. 7). Here again we find that even at 600° C. coals Nos. 11 and 3 and coals Nos. 7 and 14 approach one another very closely in the percentages of nitrogen in their tar. In all cases the percentage of nitrogen in the tar approaches a certain limit which does not differ to any extent with different coals.

Considering these results as a whole, though limited in scope and kind, we are led to believe that the nitrogen in coal exists in at least two forms—the one a less stable and the other, which is by far the greater part, a very stable form. The less stable form comes over with the tar and is closely related to it. There is no evidence to show that the tar and the more stable form of nitrogen belong to distinct molecules. On the contrary, the general behaviour of the coals, as shown by these graphs, gives strong indications that the tar and the more stable form of nitrogen originates from different parts of the same molecule—the two parts being naturally of a different structure.

Figures 9, 10, and 11 show the percentage distribution of nitrogen in the coke, tar, and ammonia at different temperatures. These graphs throw some light on another property of the nitrogen molecule in coal, namely, its stability towards heat. Thus coal No. 14 distributes the greatest percentage of its nitrogen as ammonia and in tar at 600° C. (figs. 10 and 11). Coal No. 14, therefore, decomposes most rapidly after the temperature of decomposition is reached. Coal No. 3, on the other hand, decomposes



rapidly up to 550°C. , but stops decomposing, as far as nitrogen is concerned, at this temperature, indicating greater stability of the nitrogen molecule. On further heating to 750°C. more nitrogen was found to be liberated. Steam at this temperature had no effect in liberating the ammonia. The necessary condition for such a liberation of ammonia, once the nitrogen molecule has decomposed into this stable form, is evidently a temperature sufficiently high to bring about a combination between the coke and the steam.

Evidently the nitrogen molecule decomposes in stages, as is indicated by the behaviour of coal No. 3 (fig. 9). This property suggests a case of polymerization. Frans Fischer* believes that the humic acid present in coal polymerizes during the course of its formation to form humin. It is not unlikely that this same condition exists in the resinous part of the coal, and that the intricate nature of all coals is due almost entirely to the degree of polymerization of the compounds present.

Figure 8 shows the yield of gas given off at different temperatures. There are no sudden breaks in these curves. In fact, the increase in gas is more or less gradual and consistent between these temperatures. It appears as though the gas originates from a different part of the coal altogether—probably the cellulosic portion of the coal, while the “tar-producing” portion of the coal appears to

be that part of the coal which has resulted from the final combination of those substances originating from the resins and proteins in the plant.

CHEMICAL REACTIONS.

An attempt was made to detect any secondary reactions which may have taken place between the products of decomposition of the protein in the plant by means of hydrolysing agents. But the results were negative. In all cases, however, a small percentage of the nitrogen was removed. This nitrogen was evidently NH_2 nitrogen, and in order to determine it quantitatively the following method was employed.

Twenty grammes of coal were heated under reflux for three to four hours with 300 c.c. of hydrochloric acid (1.1). The mass was filtered and the residue washed with hot water. The solution was evaporated down to a small bulk, transferred to a measuring flask and made up to 100 c.c.; 50 c.c. of this amount was Kjeldahlized to give the total amount of amido and amino nitrogen present. The remaining 50 c.c. was used to determine the amido nitrogen by distilling a known quantity in the presence of milk of magnesia. The amido nitrogen alone distils over as ammonia, which is collected in standard acid. The difference in the two results gives the amount of amino nitrogen present. Table 4 shows the results in all fourteen samples.

TABLE 4.—THE PERCENTAGE OF NITROGEN PRESENT IN COAL AS AMIDO AND AMINO ACIDS.

Coal.	Nitrogen as Amido.	Nitrogen as Amino Acids.	Total “ NH_2 ” Nitrogen.	Percentage “ NH_2 ” Nitrogen of Total N_2 .
1	·0078	·0048	·0122	·57
2	·010	·0076	·0176	·81
3	·0336	·0026	·0362	1·56
4	·020	·0094	·0294	1·35
5	·0125	·0127	·0252	1·50
6	·0124	·0125	·0249	1·54
7	·0112	·0042	·0154	·92
8	·0155	·0069	·0224	1·46
9	·0140	·0082	·0222	1·33
10	·0309	·0030	·0339	1·60
11	·0175	·014	·0184	1·14
12	·020	·0045	·0265	1·53
13	·0186	·0071	·0257	1·47
14	·010	·007	·0170	·95

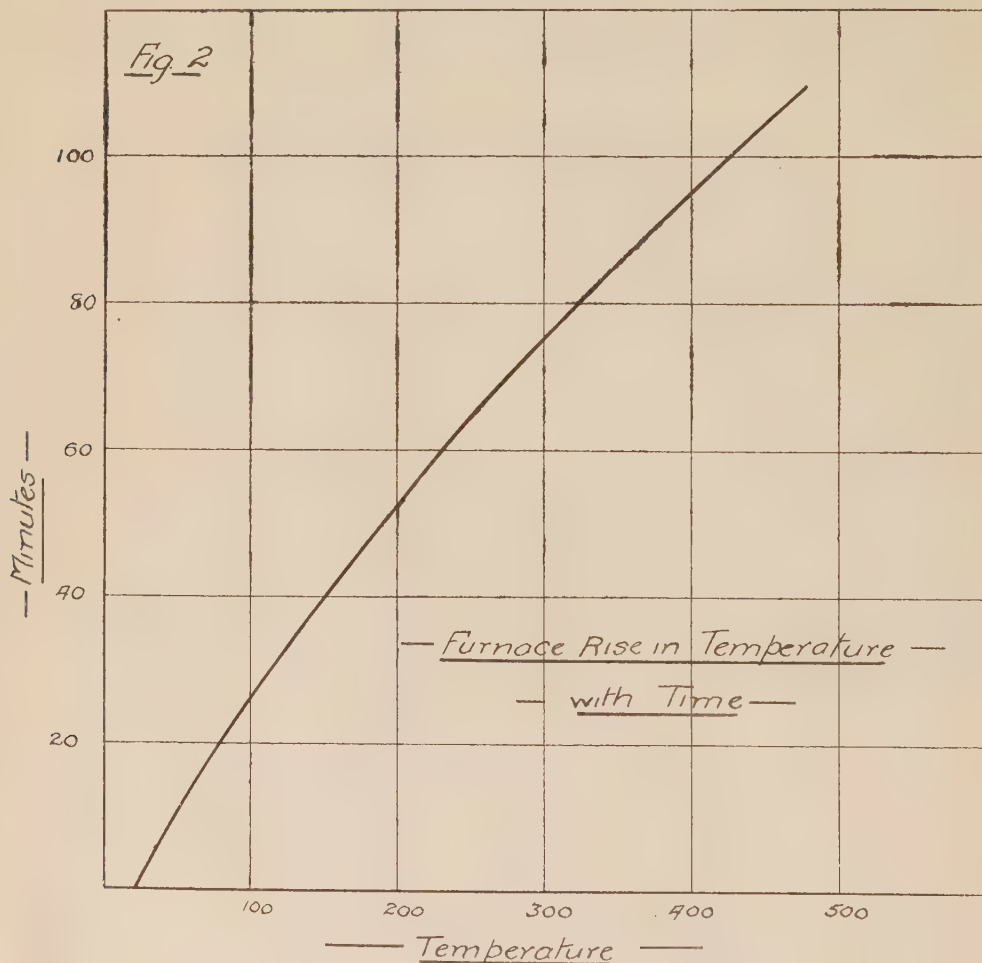
* Fischer, F., Schrader, H.: “The Origin and Chemical Structure of Coal.” *Brennstoff Chem.*, 2, 37-45 (1921).

The amounts of amido and amino nitrogen present in the coals are surprisingly low, and in order to come to definite conclusions regarding the matter an attempt was made to remove all NH_2 groupings in another way.

When carbonyl chloride is passed over heated amines a carbamic chloride is formed, which readily loses HCl to form an isocyanate.

350°C. with dry coal. The results obtained showed that only a very small portion of the nitrogen was removed.

The monamino, diamino acids and acid amides which come into the coal mass as decomposition products of the protein molecule are evidently no longer present to any extent in the coal. Consequently these compounds, during the processes of coal formation, have either



$\text{RNH}_2 + \text{ClCoCl} \rightarrow \text{RNH} \cdot \text{CoCl} \rightarrow \text{RN}=\text{C}=\text{O} + 2 \text{HCl}$. The isocyanic esters are volatile liquids with a powerful and unpleasant smell.

If coal contains amino groupings, then when CoCl_2 is passed over it at higher temperatures, we should expect the corresponding nitrogen compounds to volatilize. This was tried at 250°C. and

recombined with themselves or they have decomposed and passed off from the mass in the form of nitrogen or ammonia, thus leaving the heterocyclic compounds of the protein molecule to form the bulk of the nitrogen found in coal. It is an established fact that amino acids and acid amides will readily ammonify in the presence of bacteria in the soil. We are

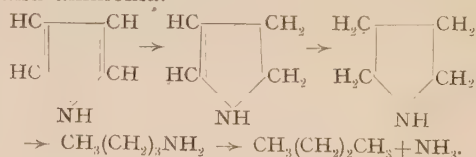
therefore more entitled to assume such a state of affairs in the case of coal than we are to assume a state of further combination. The conditions during coal formation are more favourable for such decompositions. The fact that all coals from the same locality contain amounts of nitrogen which are more or less constant, further suggests a compound which is stable to the natural agencies to which coal is exposed. The heterocyclic compounds are evidently the only portions of the protein molecule that will satisfy this condition. If this is the case, then in order to account for some of the properties of coal, we must assume that these compounds have undergone polymerization to a great and unknown extent.

Selenium Oxychloride.

As a very active solvent, the action of selenium oxychloride was tried on coal to see whether the nitrogen molecule would be affected. A colloidal mass was obtained with coal, and this mass could only be filtered by diluting the mixture with a large excess of benzene. A similar reaction was run on 500° C. coke which had all its tar constituents removed. By comparing the results it was evident that the selenium oxychloride breaks up the coal and combines with the tar-forming constituents, but does not affect the more stable form of nitrogen.

Reducing Agents.

If the stable form of nitrogen is present as pyrrol derivatives, then strong reducing agents should affect the molecule. For instance, when pyrrol is reduced, pyrroline is obtained. With strong reducing agents, such as red phosphorus and hydriodic acid, pyrroline is further reduced to pyrrolidine. This reaction, however, is not easy, for pyrrolidine is readily decomposed in the presence of these reagents to alkylamine, or still further to hydrocarbon and ammonia.



This reaction was tried on coal, using propyl alcohol and sodium, and red phosphorus and hydriodic acid. Table 5 shows the analyses of the residues obtained in both cases. Experiment 14 C was not carried out to a finish, as the retainer used in the experiment could not entirely withstand the very high pressure of the reaction. A fair amount of success was obtained, however, as can be seen from the quantity of nitrogen which was removed from the coal. The extract was steam-distilled in the presence of sodium hydroxide. The steam distillate had a strong ammoniacal odour and gave a dense red precipitate with Nessler's reagent. No amines could be detected by means of benzene sulphonyl chloride.

TABLE 5.—ACTION OF REDUCING AGENT ON THE NITROGEN IN COAL.

Treatment.	Experiment.	H ₂ O.	Ash.	N ₂ .	N ₂ on H ₂ O and Ash-free Basis.	Original N ₂ , H ₂ O, and Ash-free.
Na + C ₃ H ₇ OH.....	14 A.	3.29	10.52	1.69	1.98	2.05
HI + Phos. 180°-200°..	14 B.	1.44	14.10	1.67	1.98	2.05
HI + Phos. 250°-280°..	14 C.	1.16	30.26	1.04	1.52	2.05

SUMMARY ON THE FORM OF NITROGEN IN COAL.

The experimental data arrived at in this work suggest, though they do not prove, certain theories regarding the constitution of coal and the form in which the nitrogen exists. All past theories on coal take into account cellulosic and resinic decomposition products, and state that coal is made up of these two portions alone. This work shows that the nitrogen, or the decomposition products of protein, cannot be neglected. The nitrogen molecule is closely related to the resinic portion of coal, and forms different parts of the same molecule from which the tar originates.

Two main forms of nitrogen have been established in this work: (1) the NH_2 form, present as amino acids and acid amides, and (2) a more stable form, probably in the form of a *pyrrol* ring which has undergone polymerization. The NH_2 form does not constitute more than 1.6 per cent. of the nitrogen in the coals studied. As amino acids and acid amides readily undergo ammonification in the presence of bacteria, it is quite probable that they decompose and pass off from the coal mass during the period of formation. The heterocyclic compounds, which are present in proteins in the form of pyrrol rings, on the other hand, remain behind and account for the more or less constant percentage of nitrogen in all coals from the same locality. These pyrrol derivatives undergo polymerization to an unknown degree in the presence of the organic acids in the vegetal matter, and combine with the products of decomposition arising from the resinic matter in plants. These products of decomposition are thus present in the form of long side chains attached to the polymerized pyrrol ring. The author would suggest that this compound be called the "tar-producing portion" of the coal.

When coal is heated these side chains split off and distil over in the form of tar. The NH_2 nitrogen comes off with the tar and quite probably is present in these side chains. This accounts for the small percentage of ammonia given off

at low temperatures. When practically all of the tar has been split off, the polymerized pyrrol derivative starts decomposing in stages and liberates ammonia and hydrocarbons. In this case acetylene will evidently be formed. Part of this acetylene combines with hydrogen to form ethylene and ethane, and a further portion polymerizes to form benzene if the conditions are favourable. Finally, a stage is reached where the polymerized compound is unsaturated and at the same time unstable. At this temperature the ring breaks and a compound remains in which nitrogen is probably combined directly with carbon. When this stage has been reached the best way to obtain the nitrogen in the form of ammonia is by burning away the carbon in the presence of steam.

On these lines the presence of pyrrol and pyridine in coal-tar can be explained, since it is a distinct property of five-membered heterocyclic compounds containing nitrogen to be converted into six-membered ring compounds. Pyrrol derivatives furthermore readily polymerize in the presence of acids, and these polymerized products decompose on heating to yield ammonia. The fact that polymerized pyrrol derivatives are less stable at higher temperatures indicates that the degree and kind of polymerization which takes place during the stages of coal formation are yet unknown.

In regard to the actual behaviour of the nitrogen in the coals studied, the following conclusions are drawn:—

- (1) In distillation experiments carried out between 450°C . and 600°C . the percentage of the nitrogen remaining behind in the coke is distinct for each coal and is independent of the total amount of nitrogen in the coal. As much as 98.85 per cent. of the nitrogen remains in the coal at 450°C . in one case. In this instance only .05 per cent. of the nitrogen is liberated as ammonia. At 600°C . an average of 95 per cent. of the nitrogen remains in the coal and not more than 2.04 per cent. of the nitrogen is liberated as ammonia. On further heating to

- 750° C. in the presence of steam, an average of 70 per cent. of the nitrogen remains in the coke.
- (2) Hydrolysing agents will affect the NH_2 nitrogen in the coal, but not the more stable form.
- (3) In the coals studied the percentage of NH_2 nitrogen varied from .57 per cent. to 1.60 per cent. of the total nitrogen present. In almost all cases the greater part of this nitrogen was in the amido form.
- (4) Selenium oxychloride will react with the tar in coal and form a colloidal mass with it. It does not attack the stable form of nitrogen.
- (5) Strong reducing agents will attack the nitrogen in coal to yield ammonia. Thus red phosphorus and hydriodic acid at 250°-280° C. reduces the percentage of nitrogen from 2.05 per cent. to 1.5 per cent., calculated on the moisture and ash-free basis.
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VITA

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